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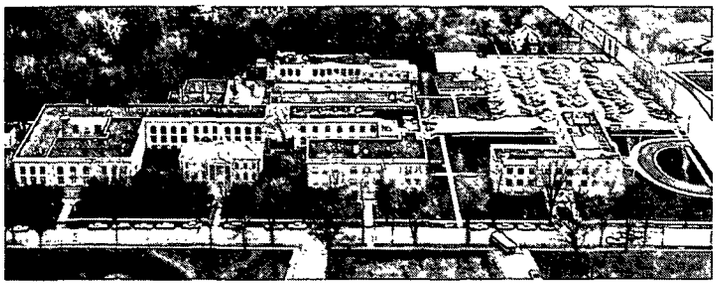

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STRUCTURAL/REACTIVITY STUDIES (I): SODA REACTIONS OF LIGNIN MODEL COMPOUNDS

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ABSTRACT

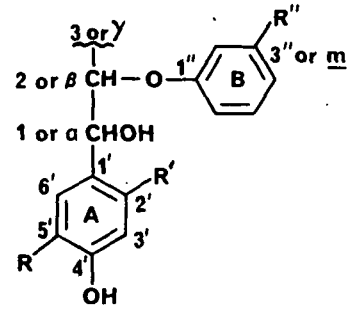
Lignin model compounds containing a phenolic "A" ring, α-OH, and β-aryl (ring "B") ether, with different substituents located on rings A and B, have been synthesized and degraded under a variety of conditions in sodium hydroxide-water (soda). Substituent changes on ring B had a large effect on fragmentation reactions of the models; changes on ring A showed only small effects. These substituent-reactivity relationships indicate that the slow step in the mechanism for model fragmentation under soda conditions is cleavage of the β-aryl ether bond. Vinyl ether formation, a reaction which competes with model fragmentation, is more prominent at low alkali concentration.

Resorcinol, a fragmentation product in one of the model degradations, was shown to be an effective promoter of fragmentation.

INTRODUCTION

Structure-reactivity studies consist of examining the rates of reaction of several closely related compounds and correlating the rate data with differences in structure in order to provide information on reaction mechanisms. We have synthesized and examined the rates of degradation of several related lignin model compounds. Our initial goal was to demonstrate the importance of electron transfer reaction mechanisms in pulping systems.[1,2] This report (soda reactions) and the one which follows (soda-additive reactions) describe our results with a structure-reactivity study of delignification mechanisms.

Two model series (1 and 2) were studied. Their definition and numbering system are given below. The term "fragmentation" refers to cleavage of the β-aryl ether bond. Substituents meta on ring B were chosen to minimize steric effects and ambiguous resonance effects. Should the B ring break off as a phenolate radical, all groups ortho and para can stabilize by resonance; the principal effect at the meta position is a simple polar effect.[3] Substituents located on the B ring would be expected to have a significant effect on reaction rates if cleavage of the β-aryl ether bond were the rate determining step in the mechanism. Substituents on the A ring would be expected to have little effect on the rate if the cleavage step were the slow step.



1, vary R'' (ring B), R=OCH_3, R'=H
2, vary R and R' (ring A), R''=CH_3 or CF_3

Synthesis

The synthetic steps used to prepare the m-substituted ring B models are given in Scheme 1. We employed two pathways to get to ketone **9**. The shorter pathway "a" has the following problems associated with it: the purification of bromoketone **6** is not practical (decomposes, lachrymator), a large excess of phenolate ion (7^-) is needed for the coupling step (otherwise **6** can polymerize with itself), and chromatography is required to purify product **9** of the excess phenol.

The longer pathway "b" allows purification of each intermediate by simple recrystallization and does not require an excess of phenol in the coupling step. This latter advantage is important

when the phenol is expensive or hard to obtain. Route "b" has worked well in some related studies in our laboratory and with the preparation of nitro model **9E**, but has been less successful with the other models. In several cases, problems arose during the coupling step; a portion of the acyl groups would transfer from **5** to **7** during the reaction, giving rise to lower yields, mixtures, and chromatography isolations. In general, the method used was path "a".

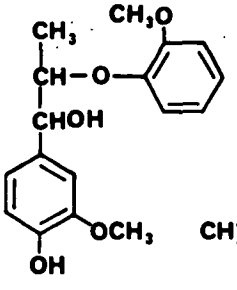
Direct reduction of ketones **9A-F** gave the non-β-methyl (or C_2) series of alcohols. Methylation of **9A-D** and their reduction gave the β-methyl (or C_3) series of alcohols. The m-OH and m-NO_2 C_3-models (**11F** and **E**) were not prepared because of both synthetic difficulties and reactivity problems. Preliminary degradations of C_2-alcohols **12F** and **E** indicated that these two model types would not be of general use for all the anticipated experiments. The nitro group was readily reduced by anthrahydroquinone (AHQ), and phenol model (**12E**) gave undesirable by-products when degraded in alkali. The abandonment of the m-NO_2 and m-OH series left us without our most and least reactive models.

The methylation of chloroketone **9B** produced an unusual result: a portion (roughly 30%) of the chloro groups were reduced, giving rise to a product mixture composed of C_2- and C_3-chloroketones **9B** and **10B**, along with the C_2- and C_3-unsubstituted ketones **9H** and **10H**. Separation of all four components of this mixture by column chromatography proved difficult. A sample containing 70% **10B** and 30% **10H** was obtained and reduced to a 70/30 mixture of C_3-chloro and unsubstituted alcohols **11B** and **11H**. The latter was subsequently studied as a mixture.

Except as noted above, the synthesis and product characterizations were straightforward (see Experimental Section). The C_3-alcohols exist as four isomers, two sets of diastereomers. Attempts to chromatographically separate these isomers were not successful. Partial separation occurred in some cases. Degradation rates of

fractions rich in one isomer were virtually identical to the rates of fractions rich in the other isomer. Therefore, from this point of view, separation of isomers is not necessary. Yet with no separation, the isomer pairs form oils which are difficult to fully purify (remove solvents, impurities, etc.) when only small amounts are available.

Another model which was examined in this study was **13**; its synthesis has already been described.[4] Simple crystallization in this case afforded a single pure isomer.



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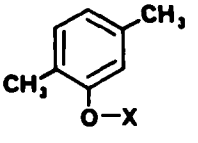
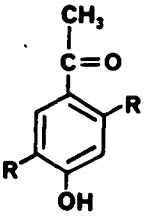


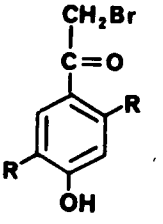
14, X = H

15, X = Ac



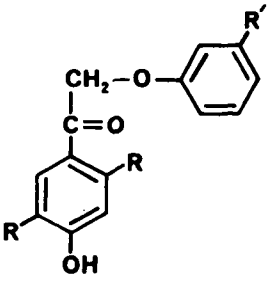
16, R = H

17, R = CH_3



18, R = H

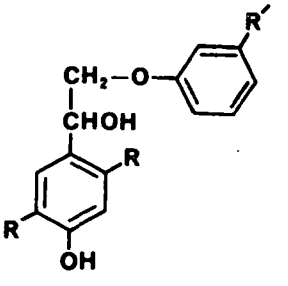
19, R = CH_3



20, R = H, R′ = CH_3

21, R = R′ = CH_3

22, R = CH_3, R′ = CF_3



23, R = H, R′ = CH_3

24, R = R′ = CH_3

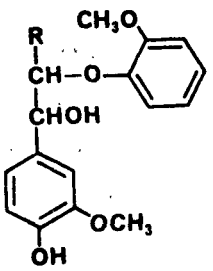
25, R = CH_3, R′ = CF_3

Two analogs of the C_2-m-methyl alcohol **12A**, having different ring A substituents, were also synthesized; these correspond to structures **23** and **24**. Model **23** was made by brominating commercially available ketone **16** to give **18**, coupling this product with m-cresol to give **20**, and reducing the latter with $NaBH_4$. The synthesis of model **24** began with acylating 2,5-dimethylphenol (**14**), followed by a Fries rearrangement of **15** to **17**, bromination to **19**, coupling with m-cresol to ketone dimer **21**, and finally $NaBH_4$ reduction. A similar sequence was used to prepare **25**, a m-CF_3 analog.

Model Selection

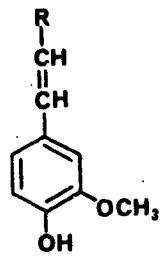
Why two sets of β-ring analogs? Our interest was initially only in C_3-models, **11**, even though their synthesis and characterization presents more problems than the C_2-models, **12**. The larger models, **11**, have the 3-carbon side chain, as does lignin, and possibly provide more reliable product analyses; their disadvantage, however, is their lack of tendency to crystallize to pure isomers.

Previous studies with C_2- and C_3-analogs **13** and **26** demonstrated the value of using the larger model.[5] Fragmentation of the C_2-model **26** by AHQ produces vinylguaiacol (**28**) and guaiacol (**29**), which in turn react somewhat with each other, thereby interfering with quantification of fragmentation. The corresponding fragments from the C_3-model **13**, namely isoeugenol (**27**) and guaiacol are stable to each other in the presence of AHQ.



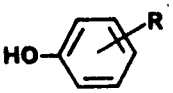
13, R = CH_3

26, R = H



27, R = CH_3

28, R = H



29, R = o-OCH_3
30, R = m-CH_3
31, R = m-Cl
32, R = m-OCH_3
33, R = m-CF_3
34, R = m-NO_2
35, R = m-CH
36, R = p-$CHMe_2$

The guaiacol recovery problem is, however, probably only limited to AHQ reactions; soda model reactions should give little, if any, styrene-type products.[6] Indeed, the C_2-*m*-R B-ring substituted models (**12**) behaved well in the soda degradations; phenol yields were reasonable and reproducible.

Models differing in substituents on the A ring would be expected to provide less information than B ring models concerning the mechanism of soda promoted fragmentation. They were, however, studied to verify the B ring model soda results and provide valuable information in the additive experiments (accompanying paper).

Phenol Analysis

A reliable analytical procedure was needed to determine the extent of fragmentation of the model compounds under varying conditions. Analysis of changes in the level of starting material (model compound) with time has many problems associated with it. For example, the model can be lost via reactions, much as enol ether formation, which are not fragmentation reactions of the β-linkage. Also, the α-hydroxy models dehydrate easily upon gas chromatography (GC) analysis. The simplest indicators of fragmentation of the model are the phenols produced.

In general, the level of ring "B" phenol (**29-33**) produced is taken to be indicative of the extent of fragmentation (or delignification).[6] In our case, some of the ring B phenols are reasonably water soluble - making quantification difficult when extraction steps are involved. We therefore sought an analytical method which could convert an alkaline phenol solution into water insoluble phenol derivatives. Two such methods were developed; each involved the use of *p*-isopropyl phenol (**36**) as an internal standard (IS).

The one method consisted of treating an alkaline aqueous phenol mixture (containing IS) with dimethylsulfate to convert phenolate

salts to methyl ethers, extracting with chloroform, and analyzing by GC. The other method involved stirring the aqueous alkaline phenol mixture containing IS with benzoyl chloride in toluene in the presence of a phase transfer catalyst, separating the organic solvent, washing, and analyzing by GC the resulting benzoate derivatives. The latter method was the most reproducible but was only successful with selected phenols. Consequently, the methylation procedure was the one employed throughout the work, and the benzoylation method was only used as a check. The agreement between methods was good.

Model Degradations - General

The lignin model compounds were dissolved in deoxygenated water containing NaOH and placed in small pressure vessels along with any additional water or water-NaOH solutions. All operations were done in a glove bag under a nitrogen atmosphere. The pressure vessels were sealed under nitrogen, rotated in a prewarmed oil bath for specific time periods, cooled, opened, and emptied. The reacted solutions were diluted with a known level of IS, dissolved in aq. alkali, derivatized by methylation or benzoation, and analyzed by GC.

Product mixtures, both before and after derivatizations, were also examined by GC-mass spectroscopy (MS). The only volatile products observed were starting materials (α-hydroxy models), vinyl ethers, the ring B phenols, and guaiacol. The latter, which is present only in small amounts, must arise from ring A by cleavage of the C_α-ring carbon bond.

RESULTS

Model Degradations - Ring B Analogs

Models **12A-D** (m-R, B ring analogs) were placed in the same reaction vessel and heated at 170°C with high levels of NaOH to

produce the data shown in Fig. 1. The initial rate of fragmentation and also the final extent of fragmentation followed the order m-CF_3 > m-Cl > m-OCH_3 > m-CH_3 for the C_2-models of the type **12**. This same order was observed at 135°C and 150°C for **12A-D** and for the C_3-models **11A-D** at 150°C; the magnitude of the differences was, however, much less at the lower temperatures. The rate and extent of fragmentation also decreased substantially at lower NaOH levels.

The data of Fig. 1 point out that there are two fragmentation processes: a fast one, occurring in the first 20 min, and a slow one thereafter. Analysis by GC-MS shows essentially no starting material was left after 40 min for both the high and low NaOH level degradations; only simple ring B phenol and cis/trans isomers of vinyl ethers remained (Fig. 2). Vinyl ether by-products have also been observed in the soda induced degradation of the guaiacyl B ring model **26**.[7,8]

These data indicate that Hβ attack by HO^- to afford vinyl ethers (**38**, path a) competes with hydroxide induced fragmentation (path b) in the first few minutes of the reaction and that, in a slower reaction (path c), the vinyl ethers also fragment (Scheme 2). The rate of vinyl ether fragmentation appears not to depend on the nature of the B ring substituent, since the rates of all four substrates are the same after about 20 min (Fig. 1).

Both vinyl ether generation and model fragmentation (paths a and b, Scheme 2) depend on hydroxide ion attack; however, fragmentation responded more to changes in the NaOH concentration. This fact has been demonstrated by complete time vs. phenol fragment yield studies (Fig. 1) and by observing phenol yields at specific times when employing different levels of NaOH. The phenol yields did not vary much when the ratio of NaOH/model were 5-25/1, but showed significant increases at the 80/1 and 150/1 ratios. Holding the ionic strength constant by the addition of NaCl had little effect. Acceleration of fragmentation of β-aryl ether models by increasing the alkali strength has also been observed by others.[7,9]

It appears that the rate of vinyl ether generation is fast and dominates at low NaOH levels. At high NaOH levels a shift in the $12^- + HO^- \rightleftharpoons 12^{-2} + H_2O$ equilibrium toward 12^{-2} probably occurs. According to Scheme 2, increasing the level of 12^{-2} in the system should favor fragmentation.

The order of reactivity at the early reaction times, namely, $CF_3 > Cl > OCH_3 > CH_3$, indicates that electron withdrawing groups aid the direct fragmentation of the models. In fact there is a good correlation between the model reactivities and the substituents' Hammett sigma values (Table 1, Fig. 3).[3]

TABLE 1

Hammett σ Values[a]

Substituent	σ_m
NO_2	+ 0.71
CF_3	+ 0.42
Cl	+ 0.37
OCH_3	+ 0.12
CH_3	- 0.17
O^-	- 0.71

[a]Groups which supply electrons have negative (-) σ values; groups which withdraw electrons have positive (+) σ values. The magnitude of the σ values reflects how well they supply or withdraw electrons.

An electron withdrawing group on ring B would be expected to favor either step (b_1 or b_2) in the proposed direct fragmentation mechanism (Scheme 2). A group such as CF_3 would favor step b_1 (base abstraction) by increasing the acidity of the α-OH proton and step b_2 (β-aryl ether cleavage) by stabilizing the ring B phenolate ion fragment.[3] The fact that the ρ-value (the slope of the 10-minute line in Fig. 3) is roughly + 0.7 argues that the cleavage step is probably the rate determining step in the sequence.

The ρ-value is a measure of the sensitivity of the reaction to ring substitution.[3] Reactions performed at elevated temperatures should be influenced less by substituent changes than those done at room temperature. Consequently, the magnitude of a ρ-value should decrease with increasing temperature. Based on the temperatures employed (170°C) in the degradations and the large distance between the meta ring substituents and the α-OH group, one would expect that the ρ-value for step b_1 of the mechanism would be less than + 0.2.[3] The observed value of + 0.7 is more in accord with the generation of a phenolate ion as the slow step, since the expected ρ-value would be about + 1.0 to 2.2 at room temperature.[3]

Besides temperature effects, the magnitude of the differences (a reflection of the ρ-value) between the substituents CF_3, Cl, OCH_3, and CH_3 could be attenuated by competing vinyl ether formation reactions. If step a_1 (QM generation) was fast and step a_2 (Cβ-proton abstraction) was slow in the sequence of reactions leading to vinyl ether products, then models with electron withdrawing groups on ring B would give rise to more vinyl ether products than models with electron releasing groups on ring B. When the rate of vinyl ether formation increases, there will be less direct model fragmentation. Thus, a CF_3 group could promote both rapid direct model fragmentation and rapid vinyl ether formation, with the latter reaction detracting from the overall potential yields of the former reaction.

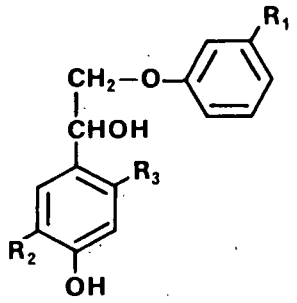
If step a_1 (QM generation) was slow relative to step a_2 (Cβ-H abstraction), substituents on ring B would have no effect on vinyl ether formation rates nor would they have any indirect effects on model fragmentation yields. Working at 143.5°C and with model **26**, Gierer and Ljunggren claim that QM formation is more rapid than Cβ-H abstraction; they observed only a slow disappearance of **26** with time.[9] Our results, using slightly different models at 170°C, do not distinguish which step is slower.

In summary, the ring B substituent-reactivity relationships establish that

- If C_β-H ionization is the slow step in vinyl ether production, the slow step in the direct model fragmentation cannot be C_α-OH ionization, since C_β-H is two bonds closer to the substituents than C_α-OH, and thus vinyl ether generation would dominate over fragmentation with groups such as CF_3.
- If quinonemethide formation is the slow step in vinyl ether production, either C_α-OH ionization or β-aryl ether cleavage can be the slow step in the direct model fragmentation.
- The sensitivity of the model fragmentation reactions to the nature of the substituents (even at 170°C) suggests that the substituent is heavily involved in the transition state of the rate determining step, which argues in favor of a slow β-aryl ether cleavage step as opposed to a slow C_α-OH ionization step.

Model Degradations - Ring A Analogs

A direct comparison of the aq. alkaline degradations of ring A model analogs at 170°C showed the following order of fragmentation efficiency: 2',5'-dimethyl-m-CF_3 alcohol **25** > 2',5'-dimethyl-m-CH_3 alcohol **24** > 3'-methoxy-m-CH_3 alcohol **12A** ≈ unsubstituted-m-CH_3 alcohol **23**. Actually, model **24** was nearly twice as reactive as the other two m-methyl analogs, with **12A** slightly more reactive than **23**. The observed reactivity differences probably reflect a combination of polar and steric substituent effects.



#	R_1	R_2	R_3
12A	CH_3	OCH_3	H
23	CH_3	H	H
24	CH_3	CH_3	CH_3
25	CF_3	CH_3	CH_3

Based on Hammett σ values and the probable importance of benzylic hydroxyl ionization to the reaction mechanism, the expected order of reactivity is 3'-methoxy **12A** > unsubstituted **23** > the two 2',5'-dimethyl alcohols **24** and **25**, assuming only polar effects operating. The unusually high reactivity of the dimethyl models **24** and **25** may be the result of a steric effect by the 2'-methyl group which retards vinyl ether and/or condensation side reactions; thus, fragmentation reactions take on greater prominence. Crowding effects on the β-carbon also enhance model fragmentation.[5]

CONCLUSIONS

The level of hydroxide used in soda treatments of m-R B ring substituted models **12A-D** dictates the course of degradation reactions taken, vinyl ether formation or direct fragmentation. The slow step in the direct fragmentation appears to be cleavage of the β-aryl ether bond. Vinyl ether by-products also fragment by a much slower reaction and by a mechanism which does not appear to be influenced by ring B substituents or alkali level.

EXPERIMENTAL SECTION

The equipment has been previously described.[10] All melting points are corrected. Most of the methods used to prepare the compounds described in this report were identical to procedures already published for very similar compounds and, therefore, will not be described here in individual detail. These methods include coupling of β-bromoketones with phenolate ions to give dimer model ketones **9A-D**, **9F**, and **20-22**;[4] methylation of dimer model ketones to give **10A-D**;[11] and sodium borohydride reduction of model ketones to give α-hydroxy models **11A-D**, **12A-F**, and **23-25**.[4]

The physical data and NMR data for the compounds prepared by standard methods are given in Tables 2-6. All the compounds in these tables showed infrared signals cm^{-1} at 3200-3400 (OH) and

typical aryl absorptions; compounds **9A-F**, **10A-D**, and **20-22** also showed 1660-1670 (C=O).

4-Acetoxy-3-methoxy-α-bromoacetophenone (5). A sample of 15.0 g of 4-acetoxy-3-methoxyacetophenone (**4**)[12] was brominated using a procedure similar to that of Erdtmann and Leopold[13] to give 9.0 g (44% yield) of colorless crystals, m.p. 85.0-87.0°C from ethanol [lit.[13] m.p. 88.0-88.5°]; IR (mull) cm^{-1} 1730 (ester C=O), 1690 (ketone C=O), and 1600 (aryl); ^{1}H-NMR ($CDCl_3$) δ 2.33 (s, 3, Ac), 3.89 (s, 3, $ArOCH_3$), 4.42 (s, 2, CH_2Br), 7.13 (d, 1, aryl) and 7.53 (s and d, 2, aryl).

1-(4'-Acetoxy-3'-methoxyphenyl)-2-(3"-nitrophenoxy)ethanone (8E). To a stirred mixture of 4.0 g (14 mmoles) of **5**, 1.5 g (9 mmoles) of KI, 3.1 g (22.5 mmoles) of K_2CO_3, and 50 mL of dry acetone was added dropwise 2.4 g (17 mmoles) of m-nitrophenol dissolved in 40 mL of anhydrous acetone. The mixture was refluxed for 3 hr, distilled to remove most of the acetone, diluted with 100 mL of water and extracted three times with 50 mL of chloroform. The $CHCl_3$ extracts were combined, washed with 0.5M NaOH and water, dried (anhydrous Na_2SO_4) and evaporated to give a solid residue, 3.8 g (80% yield). Recrystallization from benzene-petroleum ether gave crystals (61.5%), m.p. 130-133°C; IR (mull) cm^{-1} 1760 (ester C=O) 1690 (ketone C=O) and 1600 (aryl); ^{1}H-NMR ($CDCl_3$) δ 2.35 (s, 3, Ac), 3.91 (s, 3, OCH_3, 5.38 (s, 2, $-CH_2-$), and 7.14-7.93 (m, 7, aryl); MS, m/e (%), 345 (M^+, 1) 303 (12), 151 (100), 137 (4), 123 (6), 92 (3), 76 (3), and 65 (3).

1-(4'-Hydroxy-3'-methoxyphenyl)-2-(3"-nitrophenoxy)ethanone (9E). A mixture of 0.32 g (6 mmoles) of sodium methoxide, 1.75 g (5.1 mmoles) of **8E** and 20 mL of absolute methanol was refluxed for 2 1/2 hr, cooled, diluted with water and acidified with concentrated HCl to give a precipitate. The suspension was warmed and extracted while warm with $CHCl_3$. The combined warm $CHCl_3$ extracts were washed with water twice and saturated NaCl solution twice, dried (Na_2SO_4) and concentrated. The resulting precipitate was recrystallized from absolute ethanol, 0.944 g, m.p. 187.5-189.5; other physical data are given in Tables 2 and 4.

1-(4'-Acetoxy-3'-methoxyphenyl)-2-(3"-acetoxyphenoxy)ethanone (8G). The procedure used was similar to that for the preparation of **8E**, except **5** and m-acetoxyphenol[14] were used, along with a silica gel column chromatography product purification. The chromatography, with toluene and toluene-ethyl acetate elution, afforded m-diacetoxyphenol, 4-acetoxy-3-methoxy-α-iodoacetophenone (m.p. 97.5-99.5 from benzene recrystallization), and **8G** (7% yield): m.p. 103.5-105.5 (benzene); IR (mull) cm^{-1} 1760 and 1740 (ester C=O), 1710 (ketone C=O), and 1600 (aryl); ^{1}H-NMR ($CDCl_3$) δ 2.28 (s, 3, Ac), 2.34 (s, 3, Ac), 3.89 (s, 3, OCH_3), 5.23 (s, 2, $-CH_2-$), 6.65-6.86 (m, 3, aryl), 7.10-7.36 (m, 3, aryl) and 7.53-7.62 (m, 1, aryl); ^{13}C-NMR ($CDCl_3$) ppm 20.5 and 21.0 (q, Ac methyls), 55.9 (q, OCH_3), 70.6 (t, $-CH_2-$), 108.4, 111.4, 112.1, 114.5, 121.0, 122.7, and 129.6 (d, aryl), 132.7, 132.9, 144.0, 151.3, 158.4 (s, aryl), 167.9 and 168.7 (s, ester C=O) and 192.3 (s, ketone C=O); MS, m/e (%), 358 (M^+, 3), 316 (15), 274 (9), 151 (100), 137 (5), 123 (8), 93 (3), and 65 (4).

1-(4-Hydroxy-3'-methoxyphenyl)-2-(3"-hydroxyphenoxy)ethanone (9F). This compound has been obtained in two ways. The one way employed a procedure similar to the conversion of **8E** to **9E**, namely a hydrolysis of **8E** to **9F**; again solubility problems arose and the yield was low. The other procedure employed the standard coupling reaction of **6** with sodium m-acetoxyphenolate (**7G**$^-$) with chromatography work-up; small amounts of **9F** were obtained directly from the chromatography, meaning that a transesterification or hydrolysis reaction had occurred. Both procedures gave **9F** of m.p. 145-146 (benzene); physical data are given in Tables 2 and 4.

2,5-Dimethyl-4-hydroxy-α-bromoacetophenone (19). The standard bromination procedure[4] was used to convert 17.2 g of 2,5-dimethyl-4-hydroxy acetophenone (**17**)[15] to 20.2 g crystals, m.p. 129-131°C (ether) and 1.5 g of solid from evaporation of the ether mother liquor. A ^{1}H-NMR indicated that the crystals were a 70/30 mixture of **19/17**; physical data on **19** are given in Tables 2 and 4.

1-(4'-Hydroxy-3'-methoxyphenyl)-2-(3'-substituted phenoxy) ethanol (11A-D). The **11** series compounds were prepared by the

standard $NaBH_4$ reduction procedure applied to the corresponding ketone, **9A-D**. Spectral analysis of the crude products (oils) indicated that they were mixtures of diastereomers; infrared spectra showed no carbonyl absorptions and typical OH and aryl absorptions. The NMR spectra showed no carbonyl signals (i.e., 190-210 ppm in the ^{13}C) and no downfield proton aryl signals in the ^{1}H-NMR, which also showed the lack of a α-carbonyl. Their mass spectra all displayed prominent m/e 153 signals, indicative of fragmentation between C_1 and C_2 with charge retention on C_1.[16] Specific interpretations of the spectral data follow.

m-CH_3 (11A). Reduction of 2.0 g of **9A** with 2.6 g (40 equiv.) of $NaBH_4$ gave 2.3 g of oil, still containing small amounts of EtOH. Extensive evaporation removed nearly all of the EtOH. The oil is approximately a 60/40 ratio of isomers, based on ^{1}H-NMR. The oil was dissolved in warm toluene and placed on a silica gel column (2 x 38 cm). Elution of the column with 150 mL of toluene, 400 mL of 2% ethylacetate-toluene, 400 mL of 5% mixture and 250 mL of 10% mixture led to 18 fractions, which were combined into two main fractions, namely 1-7 and 8-16. The former was a 60/40 ratio and the latter a 30/70 ratio of isomers, based on ^{1}H-NMR. Comparison of the ^{13}C-NMR of the fractions allowed several of the signals to be assigned to each isomer. The ^{1}H-NMR ($CDCl_3$, δ) showed 1.10 and 1.18 (d, 3, J = 6 cps, C_3-methyls), 2.32 (s, 3, aryl methyl), 3.88 (s, 3, OCH_3), 4.3-4.7 (m, 2, C_1 and C_2 protons), 5.67 and 5.70 (s, 1, ArOH), 6.7-7.2 (m, 7, aryl) and 1.7, 2.6, 3.1, and 4.9 (broad s, 1.7, ROH and impurities). The ^{13}C-NMR ($CDCl_3$, ppm) showed 13.1, 15.8, and 21.4 (q, C_3 and aryl CH_3), 55.8 (q, OCH_3), 75.0, 77.8, 77.9, and 78.9 (C_1 and C_2 among the $CDCl_3$ signals), 108.9, 109.4, 112.9, 113.0, 114.0, 117.0, 119.2, 120.5, 122.0, 122.1, and 129.2 (d, aryl), 131.6, 132.0, 139.5, 144.8, 145.4, 146.3, 146.4, 157.2, and 157.4 (s, aryl). The MS, m/e (%), showed 288 (M, 6), 153 (100), 151 (15), 136 (42), 135 (16), 125 (21), 108 (10), 91 (26), 77 (8), 65 (20).

m-Cl (11B). A 0.60 g sample containing 60% **9B** and 40% **9H** was reduced with 0.88 g (14 equiv.) of $NaBH_4$ to give 0.74 g of oil.

The ^{1}H-NMR ($CDCl_3$, δ) showed 1.11 and 1.21 (d, J = 6 cps, 3, C_3-methyls of the diastereomers, 60/40 ratio), 3.90 (s, 3, OCH_3), 4.2-4.9 (m, 2, C_1 and C_2-protons), 5.62 and 5.69 (s, 1, ArOH, 40/60 ratio), 6.7-7.3 (m, 7, aryl) and 1.5, 2.4 and 2.9 (broad s, 1.2, ROH and impurities). The ^{13}C-NMR ($CDCl_3$, ppm) was quite complex with 13.2, 13.4, and 15.8 (q, C_3-methyls), 55.9 (s, OCH_3), nine signals at 75.0-79.2 (C_1 and C_2, plus $CDCl_3$), fifteen signals at 108.8-130.1 (d, aryl) and thirteen signals at 131.2-158.1 (s, aryl). The MS, m/e (%), showed 308 (M for **11B**, 2%), 274 (M for **11H**, 2%), 153 (100), 125 (10), 93 (25), 77 (12) and 65 (12).

[The presence of the **H** (proton) compounds in the **B** (m-Cl) compounds was not easily seen initially. There are practically no chemical shift differences for the ring A and aliphatic protons and carbons in the NMR spectra; exceptions are the carbonyl carbons of the **9** and **10** compounds. In ^{1}H-NMR, the presence of H or Cl on ring B also has little effect on the other ring B protons except, of course, the number of protons differ. The real clues that **H** compounds are in some **B** compounds come from the mass spectral differences, the ^{13}C-NMR carbonyl differences and increased numbers of signals, and in the ^{1}H-NMR phenolic hydroxyl signals and aryl integration.]

m-OCH_3 (11C). Reduction of 1.19 g of **9C** gave 1.38 g of oil, containing some ethanol (based on NMR). Attempted recrystallization from EtOH/H_2O was unsuccessful. Water was added to the recrystallization solvents and the product was extracted with $CHCl_3$. The ^{1}H-NMR showed two sets of signals which indicated that the oil was approximately a 2:1 mixture of diastereomers; these signals were at 5.76 and 5.73 (ArOH, singlets) and 1.11 and 1.19 δ (methyl doubtlets, J = 6 cps). The ^{1}H-NMR ($CDCl_3$, δ) also showed 3.77, 3.78, and 3.87 (s, 6, OCH_3), 4.3-4.7 (m, 2, C_1 and C_2 protons), 6.5-6.6 (m, 3, aryl), 6.8-7.0 (m, 3, aryl), 7.1-7.3 (m, 1, aryl), 2.6, 3.1, and 4.9 (broad s, 1^+, ROH) and residual ethanol. The ^{13}C-NMR ($CDCl_3$, ppm) showed 13.2 and 15.7 (quartets, C_3-methyls of diastereomers, 35/65 ratio), 55.2 and 55.8 (q, OCH_3), 74.8, 77.7,

and 78.7 (C_1 and C_2-carbons mixed with $CDCl_3$ signals), 102.5, 106.5, 106.6, 108.0, 108.1, 108.7, 109.2, 114.0, 119.0, 120.3, and 129.7 (d, aryl), 131.4, 131.8, 144.7, 145.3, 146.2, 146.3, 158.3, 158.5, and 160.5 (s, aryl). The MS, m/e (%), showed 304 (m, 5), 153 (100), 152 (32), 151 (32), 125 (30), 124 (19), 123 (10), 107 (17), 93 (59), and 77 (46).

m-CF_3 (11D). Reduction of 0.30 g of **9D** gave 0.28 g of oil. Recrystallization from EtOH/H_2O was not successful. The ^{1}H-NMR ($CDCl_3$, δ) showed 1.13 and 1.24 (d, J = 6 cps, C_3-methyls, ca. 60/40 ratio), 3.90 (s, OCH_3), 4.3-4.9 (m, C_1 and C_2 protons), 6.9-7.4 (m, aryl) and 2.0 and 5.6 (v. broad, hydroxyls). The ^{13}C-NMR ($CDCl_3$, ppm) showed 13.5 and 15.7 (q, C_3-methyls, ca. 30/70 ratio), 55.8 (q, OCH_3), 75.2, 77.6, 78.2, and 79.1 (C_1 and C_2 mixed in with $CDCl_3$ signals), 108.9, 109.2, 112.8, 112.9, 114.0, 114.1, 117.6, 117.8, 119.2, 120.2, and 129.8 (d, aryl), 131.2, 145.0, 145.5, 146.3, 146.4, and 157.5 (s, aryl), and 131.7 (q in coupled and decoupled spectra, C-CF_3. The MS, m/e (%), showed 342 (M, 10), 181 (11), 153 (100), 151 (9), 145 (7), 125 (14), 93 (23), and 65 (10).

Degradation Procedure. The model degradations were conducted in 4-mL capacity pressure vessels (bombs). The bombs, as many as 14 at a time, were mounted on a metal plate, which was rotated in an oil bath by means of a chain-drive system and stirring motor. The rotation could be stopped at various times to remove bombs.

The bombs were filled and sealed in a nitrogen atmosphere (glove bag). All solutions were prepared in a glove bag using deoxygenated, distilled water. All reactant solutions, IS solutions, etc., were added with an automatic pipette.

Standard solutions of sodium hydroxide and model compounds and p-isopropylphenol (IS) in aq. NaOH were prepared just prior to use. The models were present in 0.015 mmole amounts and the other reagents were adjusted to 0.015 mmole = 1 equiv.

The appropriate solutions and make-up water were added to the cool bombs. After heating for specific lengths of time, the bombs

were removed from the hot oil bath, immediately cooled in ice-water, opened, diluted with IS solution, and the contents transferred to an Erlenmeyer flask for derivatization, followed by GC analysis. Several 1M NaOH and water washes of the bombs were used to ensure quantitative transfer.

Methylation. Dimethylsulfate (1 mL, 100-350 equiv./model) was added to the product/IS mixture, and the solution was stirred rapidly for 15 min in a loosely stoppered Erlenmeyer flask. Concentrated ammonium hydroxide (4.5 mL) was thus added to quench the excess Me_2SO_4, and the solution was stirred another 15 min. Chloroform (2 mL) was added, and the solution was stirred vigorously for 2 min. The $CHCl_3$ phase was then removed with a disposable pipette, dried over Na_2SO_4 and analyzed by G.C. [Additional $CHCl_3$ extractions gave the same ratio of products to IS at a much more dilute concentration, and were thus not useful.]

Benzoylation. In this case the bombs were washed three times with 1.5 mL 1M NaOH and twice with 1.5 mL toluene. Benzoyl chloride (21 μL, roughly 5 equiv./model) and 8 mg (0.4 equiv./model) of benzyltributylammonium bromide were added to the Erlenmeyer containing the base solution, toluene and a stir bar. After stirring for 30 min, the aqueous layer was pipetted off, and the organic layer was washed twice with 3 mL 1M NaOH, twice with water, dried over Na_2SO_4, and analyzed by G.C.

Just as in the methylation procedure, reagent amounts and conditions were adjusted to give maximum, reproducible derivatization. Standard mixtures of phenols were also derivatized to give samples for determining G.C. response factors.

Analysis. Analysis of product mixtures for their phenol content was done on a 5890 Hewlett Packard gas chromatograph using a 6 foot 1/4-inch glass column packed with 3% silicone OV-17 on 100/120 chromosorb W-HP. The following temperature program was used: 65° (2 min), then 2°/min to 80° (3 min) and then 30°/min to 285° (4 min).

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TABLE 2

Selected Physical Data for Synthesized Compounds

Cpd.	% Yield[a]	m.p. (°C) Solvent[b]	Mass Spectrum, m/e (%)[c]
9A	53	170.5-172.5 (aq. EtOH)	272(M,22), 151(100), 137(5), 123(8), 108 (4), 91 (7), 77 (4), 65 (7)
9B	82	118-9 (tol.)	292/294(M,12), 151(100), 137(4), 123(9), 122(3), 111(3), 108(3)
9C	75	109-10 (tol./p.e.)	288(M,16), 151(100), 137(6), 123(10), 108(6), 92(6), 77(9), 65(5)
9D	88	107.5-8.5 (benz./p.e.)	326(M,12), 151(100), 145(14), 123(13), 108(8), 77(5), 65(7)
9E	65	187.5-9.5 (EtOH)	303(M,5), 151(100), 123(12), 122(4), 108(5), 94(3), 77(3), 76(3), 65(4)
9F		145-6 (benz.)	274(M,27), 152(9), 151(100), 137(7), 123(12), 93(5), 65(9)
10A	48	86-8 (benz./p.e.)	286(M,18), 151(100), 135(23), 123(7), 108(4), 107(4), 91(15), 77(3), 65(7)
10B		117.5-9.5	306/308(M,8), 151(100), 123(10), 111(8), 108(6), 91(8), 77(6), 65(7)
10C	32	131-2 (benz./p.e.)	302(M,28), 151(100), 123(16) 77(19)
10D	12	121-3 (tol.)	340(M,10), 152(9), 151(100), 145(6), 123(8)
12A	89	94-6 (tol.)	274(M,12), 153(100), 137(13), 125(37), 122(40), 93(56), 91(29), 77(11), 65(38)
12B	88	132-4 (tol.)	294(M,6), 154(9), 153(100), 125(13), 93(30), 65(14)
12C	85	101-2.5 (tol.)	290(M,14), 166(15), 153(100), 138(26), 137(14), 125(19), 107(10), 93(35), 77(14), 65(15)
12D	93	125-5.5	328(M,17), 154(9), 153(100), 145(10), 125(15), 93(33), 65(13)

See end of table for footnotes.

TABLE 2 (Continued)

12E	98	138-40	305(M,7), 153(100), 125(21), 110(6), 93(47), 77(9), 65(20)
12F		120-3 (benz.)	276(M,5), 153(100), 137(14), 125(33), 124(22), 110(17), 93(91), 81(22), 77(17), 65(70)
17[d]	49	131-2 (benz.)	164(M,41), 150(10), 149(100), 121(17), 91(15), 77(14), 65(6)
18[e]	23	132-3 (ether)	214/216(M,16), 122(8), 121(100), 107(10), 93(14), 77(5), 65(13)
19[e,f]	62	129-31 (ether)	242/244(M,19), 164(6), 150(10), 149(100), 135(6), 121(12), 91(14), 77(10), 65(5)
20	44	170.5-2.5 (aq. EtOH)	242(M,14), 122(8), 121(100), 107(5), 93(8), 91(6), 65(11)
21	54	188.5-90.5 (acetone)	270(M,16), 150(10), 149(100), 135(3), 121(8), 91(14), 77(10), 65(8)
22	87	191-4 (tol.)	324(M,2), 150(10), 149(100), 145(9), 135(3), 121(6), 91(12), 77(9), 65(3)
23	60	94.5-6 (tol.)	244(M,6), 136(15), 123(100), 122(45), 108(13), 95(17), 91(18), 77(18), 65(11)
24	85	100.5-3.5 (tol.)	272(M,8), 152(10), 151(100), 135(11), 123(21), 122(31), 108(10), 91(19), 77(12), 65(9)
25	75	145.5-7 (tol.)	326(M,4), 175(3), 152(10), 151(100), 145(15), 123(17), 108(7), 91(7), 77(7)

[a]All yields are of purified products, often after column chromatography and recrystallization; omitted yields were difficult to determine (i.e., materials for more than one run combined).
[b]Recrystallization solvents: benz. = benzene, tol. = toluene, p.e. = pet. ether. The lack of indicated solvent means recryst. was not performed.
[c]M = molecular ion.
[d]Known compound;[15] lit. m.p. 130-1°C.
[e]Prepared by the standard bromination procedure.[4]
[f]A 70:30 mixture, see Exp. Section.

TABLE 3

NMR Data for Ketone Model Dimers **10**[a]

Cpd.	m-R	OCH_3	ArOH	C_1	C_2	C_3	Aryl Signals[b]
10A[c]	2.26	3.89	6.23		5.40	1.69	6.6-7.2(m,5) and 7.6-7.8(m,2)
	21.5	56.0		197.6	76.6	19.4	111.0, 111.8, 114.0, 116.1, 122.2, 124.2, and 129.2(d); 126.9, 139.6, 146.8, 150.9, and 157.5(s)
10B[c]		3.90	6.29		5.42	1.69	6.65-7.25(m,5) and 7.36-7.75(m,2)
		56.0		196.3	76.6	19.1	110.6, 113.0, 113.8, 115.6, 121.3, 123.8, and 130.0(d); 126.4, 134.7, 146.5, 150.8, and 157.8(s)
10C[c]	3.83	3.91	6.24		5.43	1.72	6.8-6.9(m,5) and 7.3-7.8(m,2)
	55.1	55.9		196.9	76.3	19.0	101.5, 106.8, 106.9, 110.6, 113.8, 123.8, and 129.7(d); 126.6, 146.5, 150.6, 158.4, and 160.5(s)
10D[c]		3.93	6.13		5.49	1.73	6.9-7.4(m,5) and 7.6-7.8(m,2)
	f	56.1		196.3	76.6	19.3	110.7, 112.2, 112.5, 114.0, 117.8, 123.9, and 130.0(d); 126.5, 131.8,[g] 146.8, 151.1 and 157.4(s)

[a]Signals in δ (^1H) and ppm (^{13}C) are relative to TMS zero. While splitting patterns and integration areas are not indicated here, they were in accord with the assignments, i.e., OCH_3 appeared as a singlet (rel. area 3) in the ^1H-NMR and a quartet in the off-resonance coupled ^{13}C-NMR. Proton signals are given first, carbon-13 signals next.

[b]Numbers and letters inside the parentheses refer to relative areas and splitting, respectively: m = multiplet, s = singlet, d = doublet.

[c]$CDCl_3$ solvent. [d]Acetone-d_6 solvent. [e]DMSO-d_6 solvent.

[f]The $\underline{C}F_3$ carbon was not observed as a separate signal.

[g]The splitting remains the same in the coupled and decoupled spectra, a quartet (J = 1.3 ppm), $\underline{C}$-CF_3.

TABLE 4

NMR Data for Ketone Model Dimers **9**[a]

Cpd.	m-R	OCH_3	ArOH	C_1	C_2	Aryl Signals[b]
9A[c]	2.30	3.92	6.33		5.19	6.7-7.2(m,5) and 7.6-7.7(m,2)
	21.5	56.1		193.1	70.6	110.1, 111.5, 114.0, 115.6, 122.4, 123.4, and 129.2(d); 127.4, 139.6, 146.8, 151.0, and 158.0(s)
9B[c,d]		3.95	6.20		5.22	6.8-7.0(m,5) and 7.5-7.6(m,2)
		56.2		192.1	70.8	111.3, 114.1, 115.3, 115.5, 121.4, 123.5, and 131.0(d); 127.6, 134.8, 148.1, 152.5, and 160.0(s)
9C[c]	3.78	3.95	6.12		5.20	6.4-7.2(m,5) and 7.5-7.6(m,2)
	55.4	56.2		192.6	70.5	101.5, 106.6, 107.2, 110.1, 114.0, 123.3, and 129.8(d); 127.4, 146.8, 150.9, 159.1, and 160.7(s)
9D[c,d]		3.96	6.20		5.28	6.9-7.4(m,5) and 7.5-7.6(m,2)
	f	56.2		192.0	70.8	111.2, 112.2, 115.3, 118.0, 119.1, 123.6, and 130.8(d); 127.6, 131.8,[g] 148.1, 152.6 and 159.4(s)
9E[c]		3.96	6.06		5.28	6.9-7.0(d,1), 7.2-7.6(m,4) and 7.7-7.9(m,2)
		55.7		191.5	70.2	108.9, 111.0, 115.1, 115.6, 121.9, 122.9, and 130.4(d); 125.8, 147.6, 148.5, 152.3, and 158.5(s)
9F[c,e]	5.08	3.95	6.13		5.20	6.13(s,1), 6.4-6.5(m,3), 6.9-7.2(m,2) and 7.5-7.6(M,2)
		55.5		192.5	69.6	101.7, 105.2, 107.9, 110.9, 114.9, 122.7, and 129.6(d); 126.0, 147.5, 152.1, 158.3, and 159.0(s)

[a-f]See Table 3 for footnotes.

TABLE 5

NMR Data for Model Dimers of Type **12**[a]

Cpd.	m-R	OCH_3	ArOH	ROH	C_1	C_2	Aryl Signals[b]
12A[d]	2.32	3.90	5.65	2.80	4.99	4.03	6.7-7.2(m,7)
	21.5	56.2			72.6	74.3	110.7, 112.3, 115.2, 116.0, 119.7, 122.0 and 129.7(d); 134.1, 139.7, 146.5, 147.8 and 159.7(s)
12B[d]		3.91	7.48	4.59	4.95	4.05	6.7-7.4(m,7)
		56.1			72.4	74.6	110.6, 114.0, 115.1, 115.5, 119.6, 121.1 and 131.1(d); 133.6, 134.8, 146.5, 147.8 and 160.5(s)
12C[d]	3.78	3.91	5.64	2.75	5.04	4.02	6.5-6.6(m,3) and 6.9-7.3(m,4)
	55.4	56.2			72.5	74.4	101.5, 107.0, 107.4, 110.6, 115.2, 119.6 and 130.4(d); 133.9, 146.5, 147.8, 160.8 and 161.5(s)
12D[d]		3.92	5.66	2.69	5.07	4.08	6.9-7.5(m,7)
	f	56.2			72.5	74.8	110.7, 112.1, 115.2, 117.6, 119.1, 119.7 and 131.0(d); 131.2,[g] 133.6, 146.6, 147.9 and 160.0(s)
12E[e]		3.77	8.86	5.55	4.84	4.14	6.7-7.0(m,3) and 7.3-7.8(m,4)
		55.4			70.4	73.7	108.6, 110.3, 114.7, 115.1, 118.5, 121.7 and 130.2(d); 132.5, 145.4, 146.9, 148.3 and 158.7(s)
12F[e]	8.83	3.34	9.33	5.43	4.78	3.88	6.3-6.4(m,3) and 6.7-7.0(m,4)
		55.3			70.5	72.8	101.5, 104.8, 107.5, 110.2, 114.6, 118.4, and 129.4(d); 133.0, 145.3, 146.9, 158.0, and 159.3

a-f, see Table 3 footnotes.

TABLE 6

NMR Data for Substituted Ring A Models

Cpd.	Ar^ACH_3	Ar^BCH_3	ArOH	ROH	C_1	C_2	Aryl Signals[b]
17c	2.26 2.49		6.49			2.56	6.66(s,1) and 7.58(s,1)
	15.2 21.8				199.8	29.0	118.4 and 133.6(d); 120.8, 129.7, 139.5, and 156.9(s)
18d			9.32			4.62	6.96(d,2) and 7.95(d,2)
					189.8	32.2	115.9 and 131.8 (d); 126.6 and 162.6(s)
19c	2.26 2.49		5.49			4.40	6.67(s,1) and 7.56(s,1)
	15.6 21.8				191.5	34.8	118.8 and 134.3(d); 122.1, 126.1, 140.8, and 159.5(s)
20e		2.25	10.44			5.39	6.7-6.9(m,6) and 7.89(d,2)
		21.3			192.3	69.6	111.5, 115.1, 115.3, 121.5, 129.0, and 130.4(d); 125.9, 138.7, 157.9, and 162.4(s)
21d,e	2.27 2.41	2.22	8.90			5.23	6.7-6.8(m,4), 7.0-7.2(m,1), and 7.77(s,1)
	15.5 21.2	21.3				70.6	111.4, 115.1, 117.8, 121.2, 128.9, and 132.4(d); 121.0, 125.1, 138.6, 138.6, 157.9, and 158.8(s)

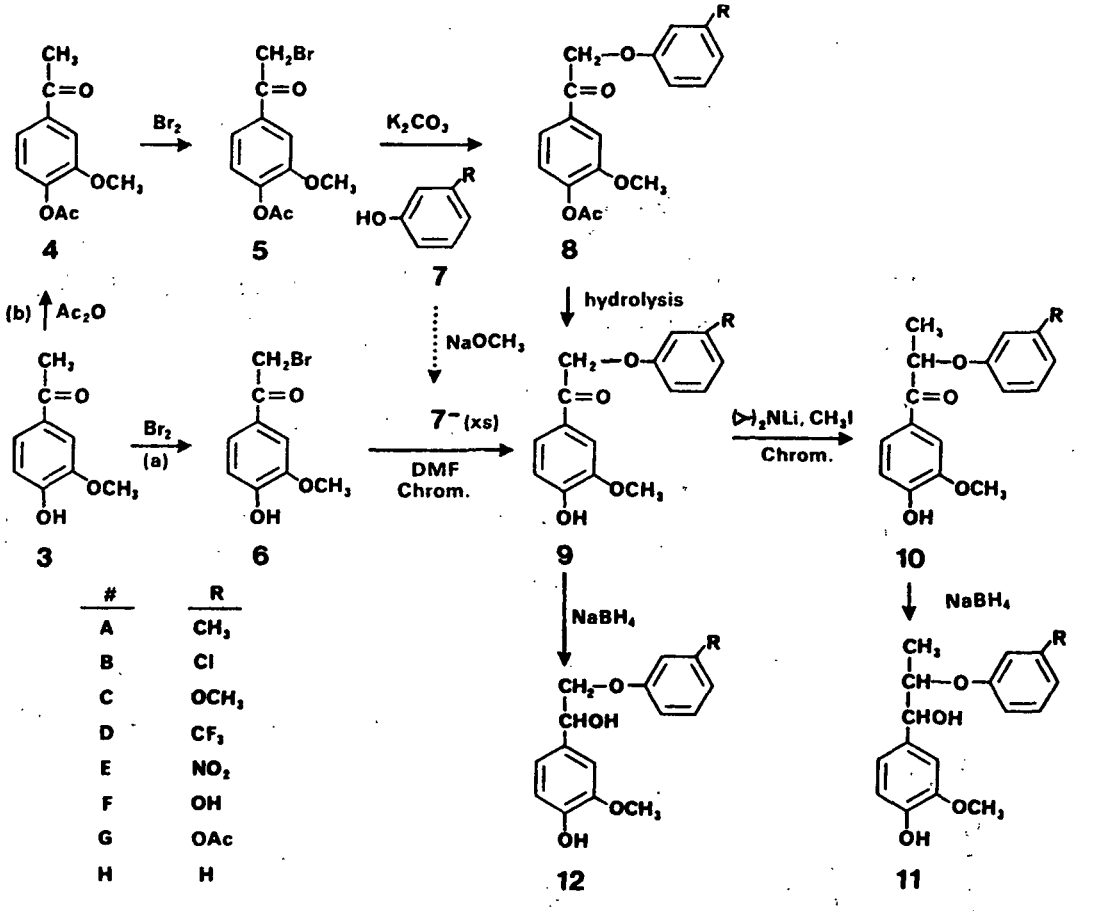
TABLE 6 (Continued)

22[d]	2.22 2.42		9.01			5.47	6.77(s,1), 7.2-7.6(m,4), and 7.82(s,1)
	15.4 21.3				193.9	70.6	110.8,[h] 116.9,[h] 117.7, 118.5, 130.2, and 132.4(d); 120.9, 124.6, 129.9,[g] 138.6, 158.1, and 158.8(s)
23[e]		2.25	9.27	5.38	4.78	3.91	6.7-6.8(m,5) and 7.0-7.2(m,3)
		21.0			70.4	72.8	111.2, 114.5, 114.8, 120.8, 127.2, and 128.8(d); 132.3, 138.5, 156.2, and 158.2(s)
24[c,d]	2.26 2.31	2.21	5.33	2.84	5.25	3.96	6.53(s,1), 6.7-6.8(m,3), and 7.1-7.3(m,2)
	15.8 18.7	21.4			69.0	73.4	112.1, 115.8, 116.8, 121.8, 129.3, and 129.6(d); 121.8, 130.9, 133.8, 129.5, 154.7, and 159.5(s)
25[d]	2.17 2.27		8.02	4.51	5.22	4.09	6.63(s,1) and 7.2-7.6(m,5)
	15.9 18.7				68.7	73.8	112.0,[h] 117.0, 117.6,[h] 119.1, 129.3, and 131.0(d); 122.0, 130.4, 131.6,[g] 133.9, 154.9, and 159.8(s)

a-f, see Table 3 footnotes.
[g]Fine doublet (J = 0.2 ppm) in the decoupled spectrum; signals probably correspond to C_2" and C_4".

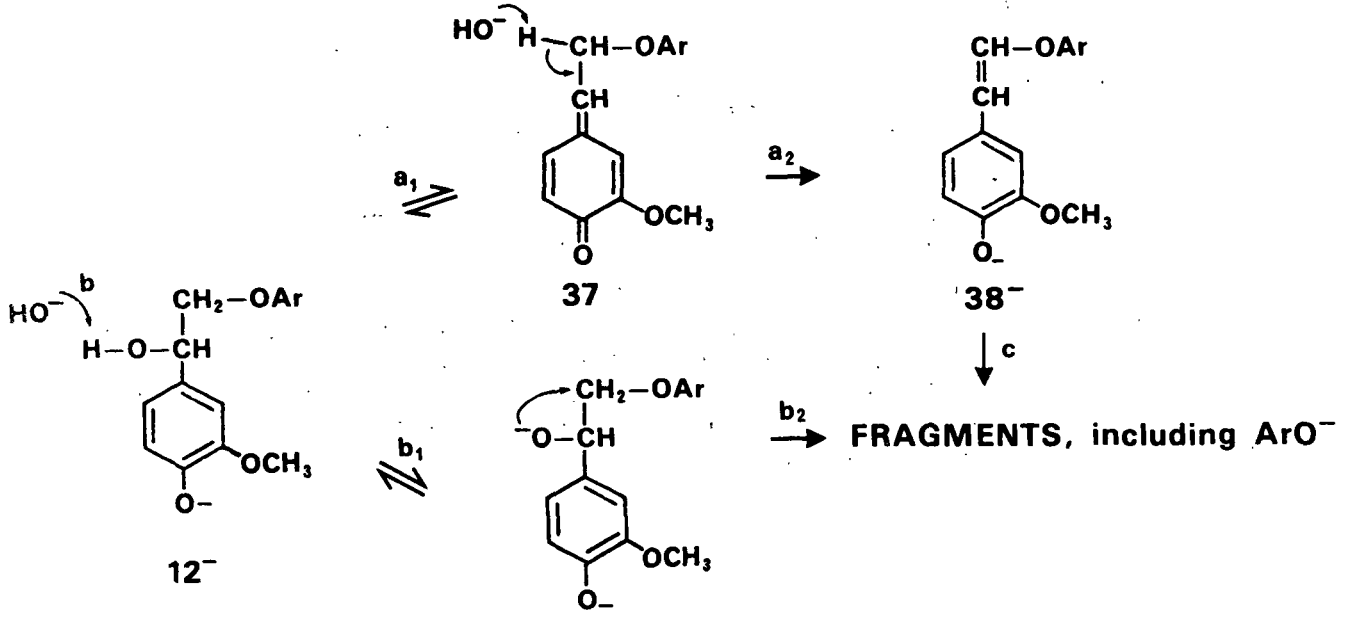
SCHEME 1

Steps in the Model Syntheses



SCHEME 2

Modes of Soda Induced Decomposition of Models 12



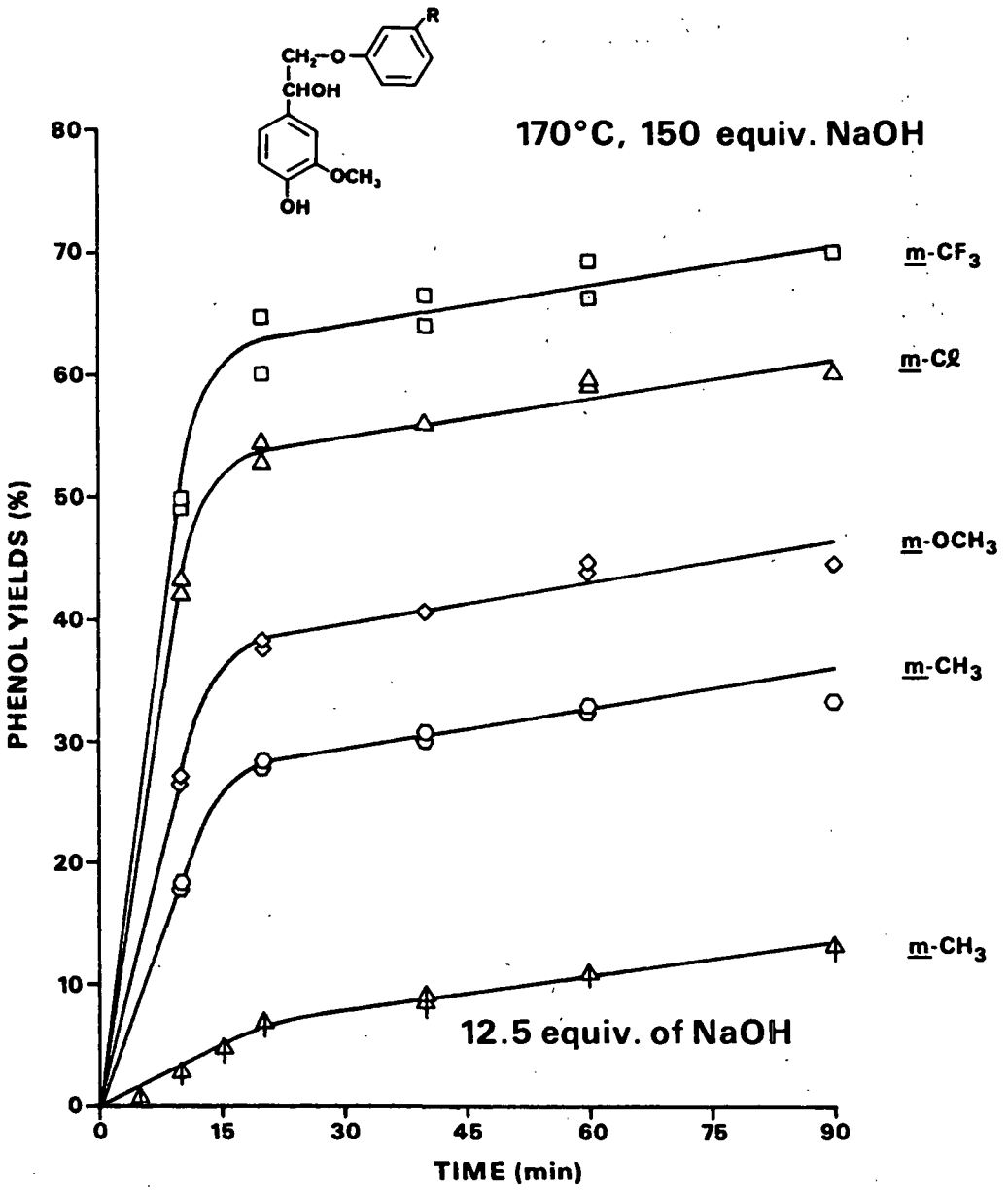


Figure 1. Phenol yields as a function of time in the simultaneous degradation of models **12A-D** at 170° in the presence of 150 equivalents of NaOH (upper four curves) and the single degradation of **12A** at 170° with 12.5 equiv. of NaOH (lower curve).

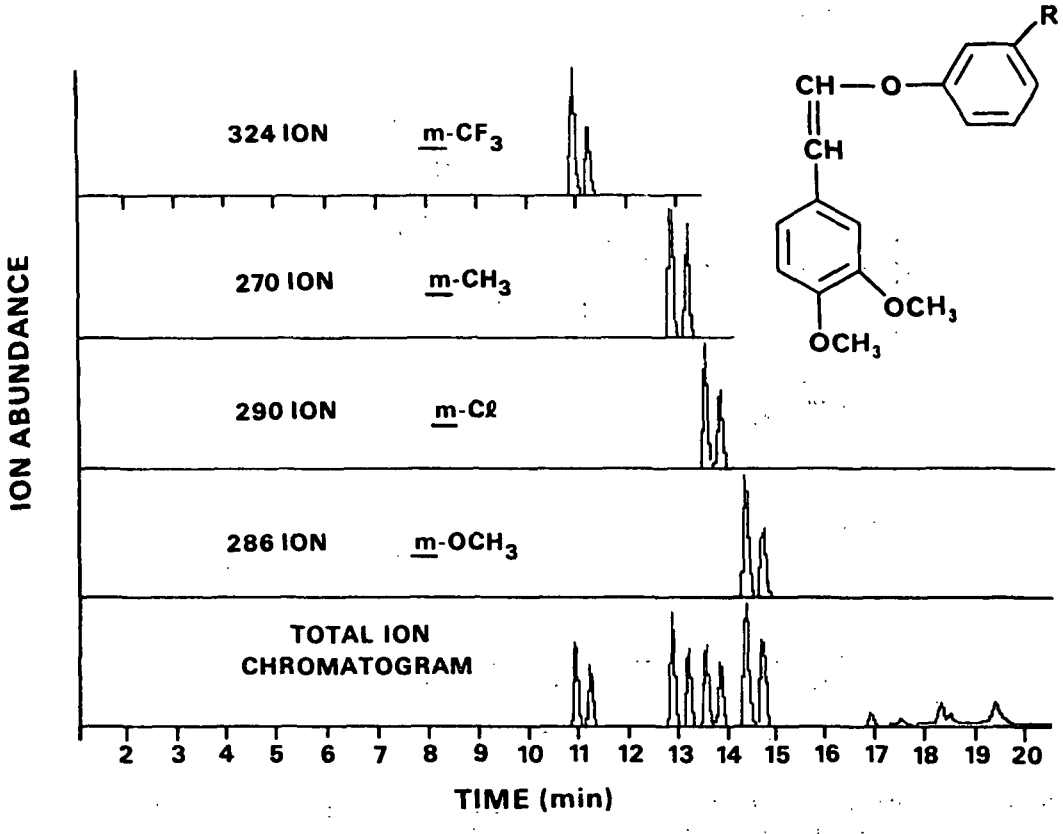


Figure 2. GC-MS analysis of the 40 minute methylated product mixture from the simultaneous degradation of models **12A-D** at 170° with 150 equiv. of NaOH. Ion selection (top portion of the figure) shows the various cis/trans vinyl ethers (**38**) derived from **12A-D**. The bottom portion of the figure displays the total ion chromatograph; early signals due to phenol fragments are not present because of a time delay which was used in the analysis and the later signals correspond to dimers of vinyl guaiacol (**28**).

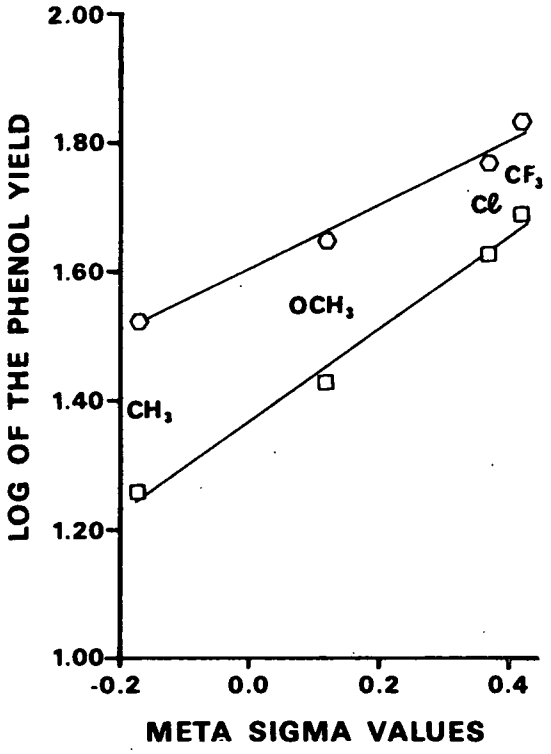
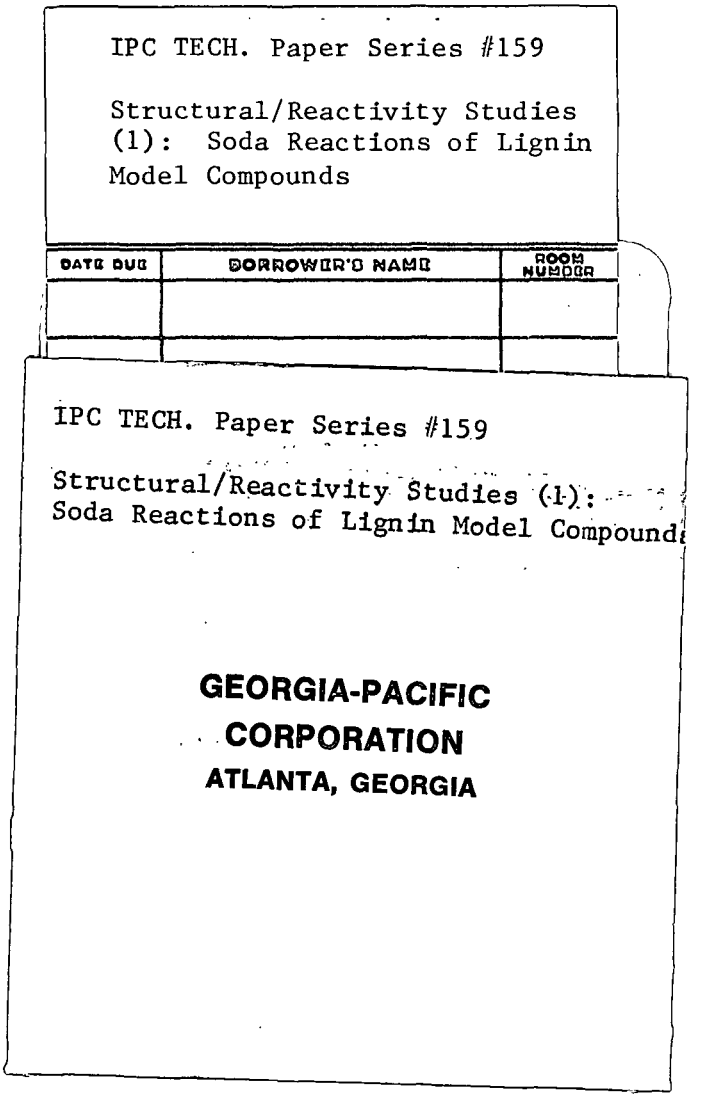


Figure 3. Correlation of σ_m values with the log of the phenol liberation yields obtained from Fig. 3: □ , 10 min yields; ⬡, 60 min yields.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